

Ferromagnetism in $2p$ Light Element-Doped II-oxide and III-nitride Semiconductors

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Abstract

II-oxide and III-nitride semiconductors doped by nonmagnetic $2p$ light elements are investigated as potential dilute magnetic semiconductors (DMS). Based on our first-principle calculations, nitrogen doped ZnO, carbon doped ZnO, and carbon doped AlN are predicted to be ferromagnetic. The ferromagnetism of such DMS materials can be attributed to a p - d exchange-like p - p coupling interaction which is derived from the similar symmetry and wave function between the impurity (p -like t_2) and valence (p) states. We also propose a co-doping mechanism, using beryllium and nitrogen as dopants in ZnO, to enhance the ferromagnetic coupling and to increase the solubility and activity.

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Magnetic $3d$ transition metal ($3d$ TM) doped dilute magnetic semiconductors (DMS) based on III-V and II-VI hosts have been extensively studied due to their potential applications in spintronics [1]. However, despite considerable theoretical and experimental efforts, the origin of ferromagnetism observed in some DMS is still under debate, and whether the ferromagnetic (FM) property arises from the doped magnetic TM ions which were observed to form magnetic clusters or secondary phases is still not clear. These extrinsic magnetic behaviors are undesirable for practical applications. A possible way to avoid problem related to magnetic precipitate is to dope semiconductors or oxides with nonmagnetic elements instead of magnetic TM. Following this idea, room temperature ferromagnetism has been demonstrated in Cu and Ti doped GaN [2, 3] and ZnO [4, 5]. Besides cationic impurities, theoretical studies predicted that anion substitutions in IIA-oxide can also lead to ferromagnetism [6, 7]. This represents a new concept in the search for potentially useful DMS. Work done so far along this line have been confined to IIA-oxides, and the mechanism for ferromagnetism in such anion doped magnetic materials is still not understood. The existing theories of DMS cannot be applied because they are based on d and f orbitals but there are no such orbitals in these anion doped materials. There are several important differences between the $2p$ and the $3d$ orbitals which determine the different magnetic properties of DMS doped with $2p$ LE (anion) and $3d$ TM (cation). Firstly, the anion $2p$ bands of the light element are usually full in ionic states, leaving no room for unpaired spins compared to $3d$ bands of TM. Secondly, the spin-orbit interaction of p states is considerably reduced compared to that of d states since it scales with the fourth power of the atomic number. Consequently, spin relaxation of DMS doped with $2p$ light elements is expected to be suppressed by up to two orders of magnitude in comparison with $3d$ cation doped DMS [8]. Thirdly, valence electrons in p states are more delocalized than those in d or f states and have much larger spatial extensions which could promote long-range exchange interactions. Therefore, Despite suffering from low solubility[9, 10, 11], DMS doped with $2p$ light elements can be weak ferromagnets in a highly ordered and low doping concentration.

In this letter, we present a possible pathway toward novel II-oxide and III-nitride DMS based on doping by $2p$ LE and explore the origin of their ferromagnetism. Wide band gap II-oxide and III-nitride semiconductors, such as ZnO and AlN, which have been widely investigated both theoretically and experimentally for applications in optoelectronics, are potential host materials for DMS. Results of our first-principles calculations predict that

nitrogen doped ZnO (ZnO:N), carbon doped ZnO (ZnO:C), and carbon doped AlN (AlN:C) are ferromagnetic. Surprisingly, almost all magnetic moments reside on the p -states of anions (C, N, or O). Compared to the conventional 3d TM cation doped DMS, these 2p LE anion doped DMS can provide a possible way to resolve the clustering problem of magnetic elements and will open another avenue for producing potentially useful DMS. Since these DMS typically have a low doping concentration but enough mobile carriers, and only 2p electrons of dopants and hosts contribute to the magnetism, the origin of ferromagnetism in these materials challenges our current understanding of ferromagnetism of DMS. Therefore, a comprehensive understanding of the physics of 2p LE anion doped DMS is essential for further exploration of new DMS. We provide a physical insight into the ferromagnetic mechanism of such DMS.

In addition, we propose a co-doping mechanism to enhance the ferromagnetism of 2p LE doped DMS materials. Such an approach has been used to solve the asymmetry doping problem of ZnO. For example, a co-doping approach [12] was demonstrated to be effective in enhancing the N solubility and reducing the ionization energy of ZnO:N-based materials, such as ZnO:N+Ga and ZnO:N+Be [13, 14]. Recently, it was found that ferromagnetism in DMS can be enhanced by co-doping. For example, Sluiter *et al.* used this approach to promote the FM state and increase the Curie temperature (T_c) of ZnO-based ferromagnets [15]. Based on results of our first-principles calculations, we predict that FM coupling in ZnO:N can be enhanced by co-doping with Be, and for the first time, we propose that N doped ZnO has possible application in spintronics, besides optoelectronics which has been studied extensively.

We performed band structure and total-energy calculations using first-principles method based on the density functional theory. The calculations were carried out using the VASP program [16], with the generalized gradient approximation [17], and projector augmented wave method. The energy cutoff was 400 eV and a k -mesh of $2\times2\times2$ was used for a 108-atom ZnO host supercell ($3a\times3a\times3c$). All atoms were allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.02 eV/Å.

We consider first a single anion-substitution (N_O) which is modeled by replacing an oxygen atom in the supercell by a nitrogen atom. This corresponds to a doping concentration of 1.85 at.%, comparable to experimental doping level. Based on the calculated total-energy, N_O favors a spin-polarized state and its total energy is 23 meV lower than that of the non-

spin-polarized state. Each N dopant introduces a total magnetic moment of $1.0 \mu_B$ ($\sim 0.4 \mu_B$ from N itself, $\sim 0.4 \mu_B$ from its twelve second neighboring O atoms, and $\sim 0.1 \mu_B$ from its four nearest neighboring Zn atoms). Fig. 1(a) and 1(b) show the calculated total density of states (DOS) and partial density of states (PDOS) of the $2p$ states of nitrogen and a second nearest neighboring oxygen, respectively. As can be seen, the N $2p$ states overlap significantly with those of O $2p$ near the Fermi level, suggesting a strong interaction between them. This strong interaction results in the splitting of the energy levels near the Fermi energy. The spin-up states are fully occupied but spin-down states are partially filled. The corresponding spin density distribution is shown in Fig. 2(a). Different from $3d$ TM-doping in wurtzite host semiconductors where the spin is exclusively localized in a tetrahedron formed by the four nearest neighboring anions of an impurity $3d$ cation[2], much of the spin density in the N doped ZnO are localized on the dopant itself and its twelve second neighboring O anions, with a minor contribution from the nearest neighboring Zn atoms. Therefore, the magnetic moment in N doped semiconductors is mainly contributed by the anions, and it results mainly from the delocalized $2p$ orbitals. The large spatial extension of the $2p$ states can be clearly seen in Fig. 2(b).

To investigate the magnetic coupling between N impurities, a pair of N atoms are incorporated into the same ZnO supercell by substituting two O atoms which are separated by 3.249 Å, 6.136 Å, and 9.252 Å, respectively. This corresponds to a doping concentration of 3.7 at.%. Results of our calculations show that the magnetic moments of the two N dopants favor FM coupling in each of the three configurations and the energy of the FM state is 7 meV, 22 meV, and 10 meV lower than that of the corresponding antiferromagnetic (AFM) state, respectively. This indicates that ZnO:N is a weak ferromagnet in a low nitrogen concentration. Fig. 3 shows the magnetic coupling between the two N ions separated by 6.136 Å. As can be seen, charge carriers localized around the anions between the N ions are polarized and have the same spin orientation as that of the N ions. Consequently, these polarized charge carriers mediate the long-range ferromagnetic coupling between the N ions.

Similar spin polarization was also found in C doped AlN and ZnO. Fig. 1(c) and 1(d) show the total DOS of AlN:C and ZnO:C. The calculated magnetic moments per carbon dopant are 1.0 and $2.0 \mu_B$ in AlN:C and ZnO:C, respectively. The spins also mainly reside on the C dopant and its neighboring N or O atoms. Both systems energetically favor the FM ground state. High Curie temperature (over 400 K) ferromagnetism in C doped ZnO

has been demonstrated recently[10].

Although no theoretical consensus on the mechanism of ferromagnetism in DMS has been reached, it is now well established that spin-polarized carriers (holes or electrons) are crucial for the ferromagnetism in DMS, either free or localized. Such an understanding of FM origin can be based on band structure models [1, 18, 19]. If the localized d states of impurities reside in the band gap of GaN- and ZnO-based DMS, the double-exchange interaction, competing with the antiferromagnetic super-exchange interaction, is responsible for the dominant ferromagnetism [18]. However, both double- and super-exchange interactions cannot account for the long-range magnetic order at low doping concentrations of a few percent. On the other hand, if the d states of the impurity states are within the valence band, such as in GaAs:Mn, it was confirmed both theoretically [1] and experimentally [20] that ferromagnetic correlations of impurity ions are mediated by free carriers via a strong p - d hybridization exchange interaction. Additionally, some studies in the opposite limit of strongly localized carriers, which are bound to impurity bands, known as bound magnetic polarons have been proposed [21]. These theories have been used, to some degree of success, to explain the ferromagnetism in 3d or 4f TM doped DMS. However, for the 2p LE doped DMS, the mechanism should be different since such materials have special magnetic properties such as long-range FM coupling, high hole concentration, and only p orbitals contribute to the magnetism.

Here, we propose that alignment of magnetic moments in 2p LE doped DMS is achieved through a p - d hybridization-like p - p coupling interaction between the impurity p states and the host p states at the top of the valence band. This interaction follows essentially from quantum mechanical level repulsion, which “pushes” the minority state upward, crossing the Fermi level [see Fig. 1(a)]. Consequently, the p states split into more stable threefold t_2 states which are either fully occupied or completely empty. The symmetry and wave function (p -like t_2) of the impurity 2p state are similar to those of the top valence band of the III-nitride and II-oxide which consists mostly of anion p orbitals. Therefore, a strong p - p coupling interaction between the impurity state and valence band state is allowed near the Fermi level. Substitution of C for N in AlN or C/N for O in ZnO introduces impurity moments as well as holes. Different from Mn ions in GaAs:Mn which polarizes spin of holes in opposite direction, the spin density near each anion impurity in 2p LE doped DMS tends to align parallel to the moment of the impurity ion under the p - p interaction, as illustrated

in Fig. 3(a) and Fig. 4(a). The strong p - p interaction leads to stronger coupling between impurity and carrier spin orientations. Sufficiently densed spin-polarized carriers are able to effectively mediate an indirect, long-range ferromagnetic coupling between the $2p$ LE dopants, as illustrated in Fig. 4(b). The spatially extended p states of the host and the impurity are able to extend the p - p interaction and spin alignment to a large range and thus to facilitate long-range magnetic coupling between the impurities. This model gives a reasonable explanation to the experimentally observed ferromagnetism in ZnO doped with a small amount of carbons [10]. Therefore, it is the p - p coupling interaction that determines the electronic and magnetic properties of $2p$ LE doped DMS, and free carriers play an essential role in mediating the spin alignment in such DMS.

N has limited solubility in ZnO (1%–3%) [9, 11] and ZnO:N is expected to be a weak ferromagnet. To increase the N solubility and enhance ferromagnetism in ZnO:N, we propose a co-doping approach. The conventional co-doping concept was proposed by Yamamoto and Katayama-Yoshida [12] to solve the problem of doping asymmetry in ZnO. Two acceptors are combined with a donor or an isovalent impurity to form an acceptor defect complex. By choosing the co-doping element carefully, the acceptor defect complex can increase the solubility of the desired dopants and reduce the acceptor defect level. Following this concept, Be-N co-doped ZnO was demonstrated, both theoretically and experimentally, to be a promising p -type ZnO [22, 23]. The concentration of N dopants was increased from 1% to 7% with 4% Be co-doping [23]. Furthermore, the ionization energy of the N dopants was reduced from 0.4 eV in ZnO:N [24] to 0.12-0.22 eV in Be-N co-doped ZnO [22].

Besides its high solubility in ZnO, Be was chosen as a candidate for co-doping of ZnO:N in the present study because it is nonmagnetic and it does not have its own p electrons. Therefore it would not interfere with the magnetic ordering in ZnO:N. Based on the experimental ratio of Be to N concentration [23] and the co-doping theory, a defect complex consisting of one Be atom and two nitrogen atoms (Be+2N) is considered. Results of our first-principles total-energy calculations indicate that the most stable configuration of the Be+2N defect complex in ZnO is a N-Be-N structure in which the Be atom, substituting a cation, is between two satellite N atoms occupying the nearest-neighboring O sites, similar to the Ga+2N complex in ZnO [13]. The calculated ionization energy of this complex is 0.2 eV which is in good agreement with results of earlier DFT-LDA calculations (0.12-0.22 eV) [22]. More importantly, this value is smaller than that of ZnO:N (0.4 eV) [24]. Furthermore,

our calculations show that the co-doping with Be stabilizes the FM state within the same structure. The FM state of the two N dopants in the Be+2N defect complex is energetically favored over the AFM state by 54 meV which is larger than that of the same configuration but without Be co-doping (7 meV). The enhancement of the FM state in ZnO:Be+2N may be attributed to the decrease in the ionization energy of ZnO:N and lowering of the acceptor level by co-doping. This leads to an increase in carrier concentration and enhancement of the *p-p* coupling interaction. It is noted that both effects play a key role in the FM coupling of the *2p* LE doped DMS. Moreover, the ZnO:Be+2N can be expected to have a higher Curie temperature than ZnO:N due to the enhanced *p-p* coupling interaction in the former[1].

In summary, *2p* LE doped II-oxide and III-nitride semiconductors were studied and are proposed to be potential candidates for novel DMS materials, which broadens the horizon of currently known magnetic systems. Based on results of our first-principles calculation, we propose *p-p* coupling interaction as the origin of ferromagnetic coupling in such DMS. Furthermore, Be co-doped ZnO:N was investigated as a possible approach to stabilize and enhance the FM state of ZnO:N. It would be interesting to grow these materials experimentally and to explore their applications.

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FIG. 1: (color online) Total DOS (a) and partial DOS (b) of N doped ZnO and total DOS of C doped AlN (c) and C doped ZnO (d). One dopant is incorporated into the 108-atom supercell which corresponds to a doping concentration of 1.85 at.%. The Fermi energy is set to zero.

FIG. 2: (color online) The spin-density (a) and charge-density (b) of N doped ZnO. Most of the spin density is localized on the doped N atom and its twelve second neighboring O atoms. The spin density around the nearest neighboring Zn atoms which are not in the plane shown here is much smaller.

FIG. 3: (color online) The spin density due to two N dopants separated by 3.136 Å. (a) FM coupling and (b) AFM coupling. The FM state is most stable than the AFM state. Blue and green isosurfaces correspond to up and down spin densities, respectively.

FIG. 4: (color online) Schematic diagram showing ferromagnetic coupling between spins of doped N impurities. (a) The magnetic moment of N polarizes carriers and aligns the spins of the carriers in the same direction as that of the N dopant. (b) If the carrier concentration is sufficiently high, it is able to effectively mediate indirect ferromagnetic coupling among nearly all doped N ions due to the long ranged $p-p$ interaction. Cation are not shown in the diagram.

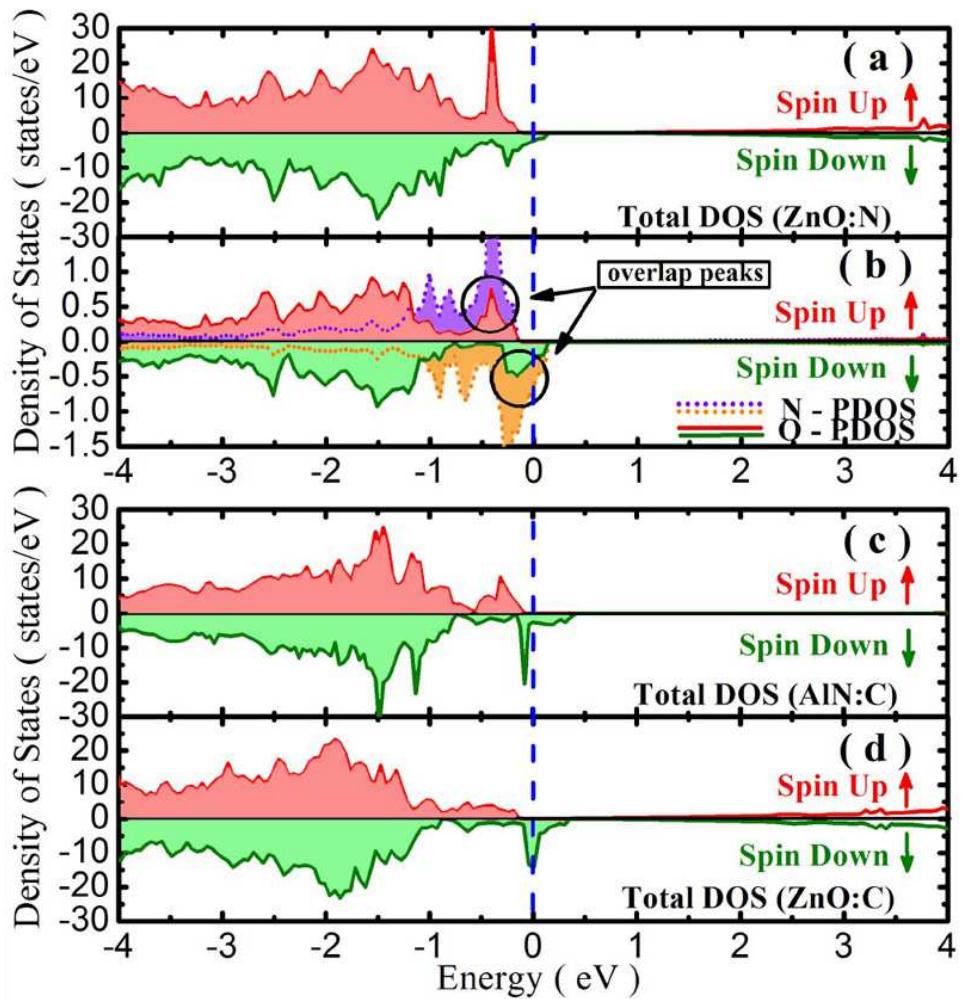


Fig.1 Shen et al.

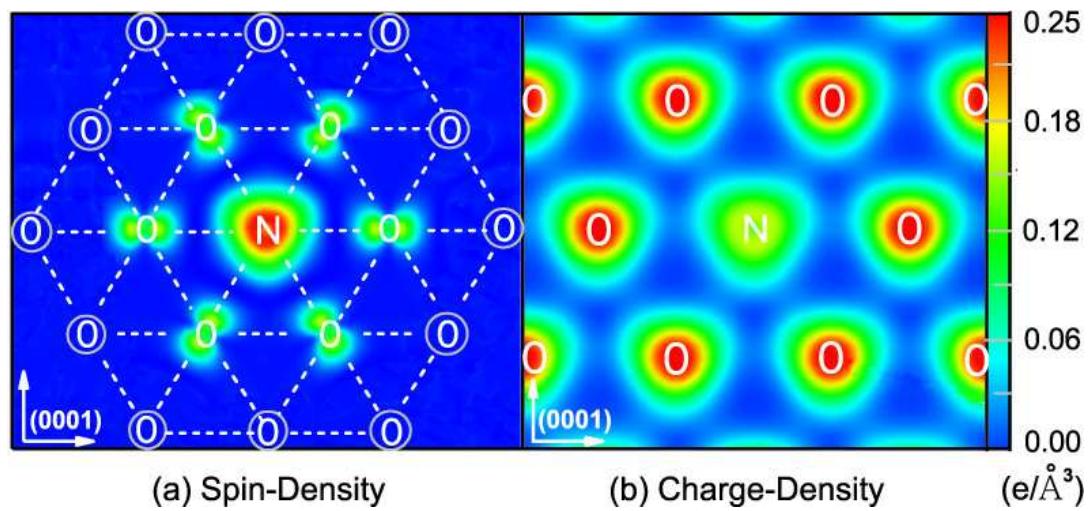


Fig.2 Shen et al.

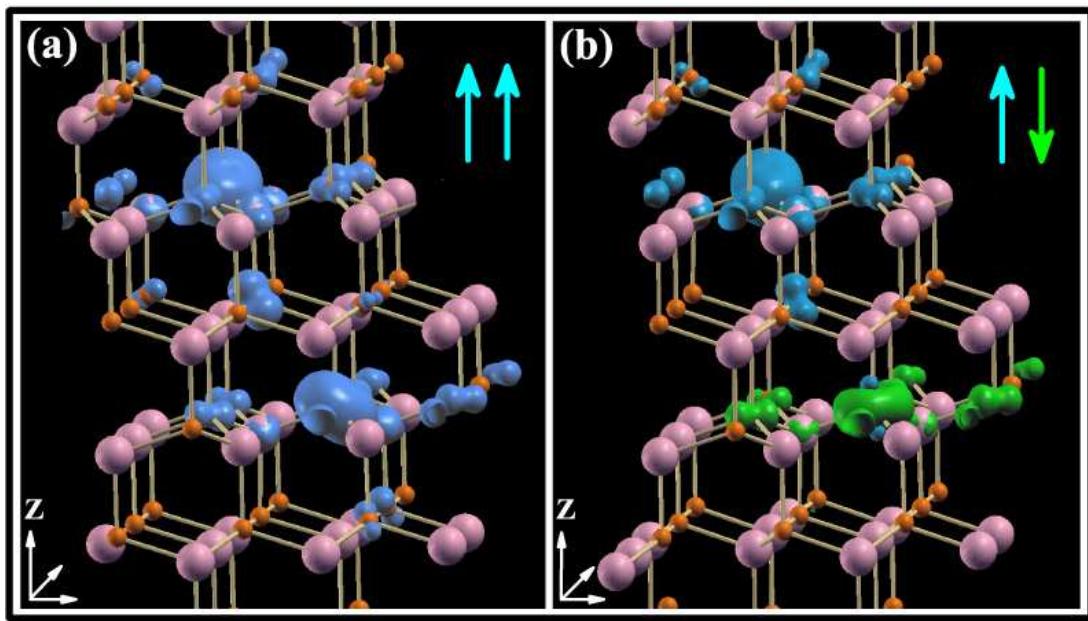


Fig.3 Shen et al.

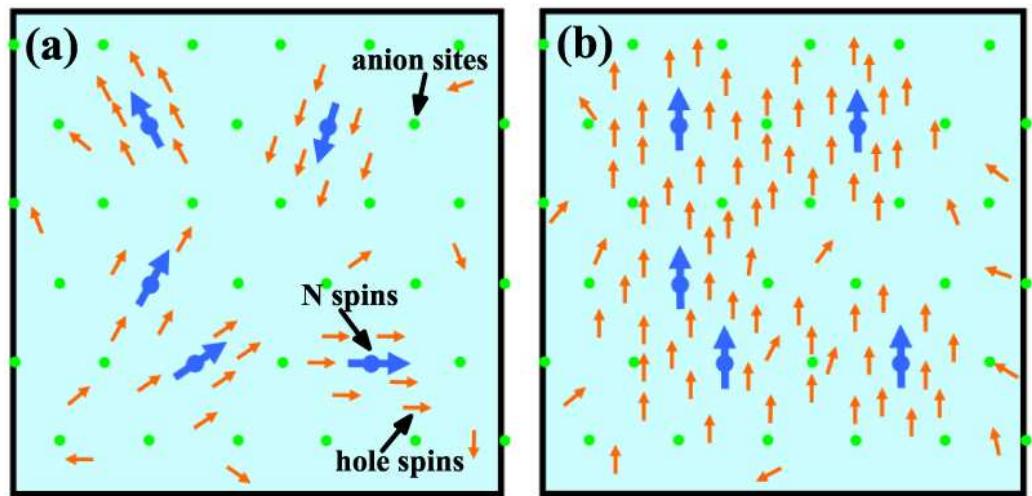


Fig.4 Shen et al.